



Short communication

A cocrystallized catalyst-coated membrane with high performance for solid polymer electrolyte water electrolysis



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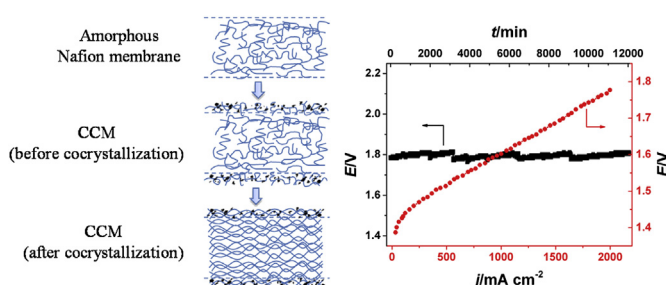
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HIGHLIGHTS

- Amorphous Nafion membrane and catalyst layers were crystallized together.
- Reinforced bonding between membrane and catalyst layers.
- Voltage of water electrolysis was 1.777 V at 80 °C and 2 A cm⁻²
- Cocrystallized catalyst coated membrane exhibited high stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A cocrystallized catalyst-coated membrane (CCM) is prepared by together heating amorphous Nafion membrane and catalyst layers at 120 °C to develop the membrane electrode assembly for solid polymer electrolyte (SPE) water electrolysis. The cocrystallization treatment effectively reinforces the bonding between membrane and catalyst layers, and increases the hydrophobicity of the catalyst layers. The SPE water electrolyser with the cocrystallized CCM decreased cell voltage by 0.09 V at 2000 mA cm⁻² at 80 °C and improved the stability in comparison with the conventional CCM.

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1. Introduction

Solid polymer electrolyte (SPE) water electrolysis is a promising method for hydrogen production especially from renewable energy sources [1–4]. Compared with the conventional alkaline water electrolyser, SPE water electrolyser possesses the advantages of

safety, simplicity, high energy efficiency, high specific production capacity and low maintenance [3].

Membrane electrode assembly (MEA) is the key component of SPE water electrolyser. However, the recent works on SPE water electrolysis have been mainly focused on catalyst [5–7]. To the best of our knowledge, reports on the research and development of MEAs have been very limited [8–10]. At present, the preparation of MEA for SPE water electrolysis is similar to that for proton exchange membrane fuel cell, and most of the MEAs have been prepared by the catalyst-coated membrane (CCM) method [11–13]. Compared

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with the gas diffusion electrode, the CCM has been demonstrated to have lower catalyst loading, thinner and much more hydrophilic catalyst layers [11]. However, the catalyst layers of the CCM are prone to peel off from the membrane for the following reasons: (1) the different swelling degrees between membrane and catalyst layers in water, (2) large amount of gas generation in catalyst layers during water electrolysis, and (3) nonuniformity of compression force between the land and under the channel [14,15]. In addition, the complete hydrophilicity of catalyst layers of CCM makes against the gas transmission, thus decreases the utilization ratio of the catalysts [9]. To increase the adhesion of the electrode to the membrane, Millet et al. [16] chemically reduced noble metal cationic species within Nafion membrane. However, CCM fabricated by this method had large catalyst particle size and high catalyst loading, and was prone to induce H_2 and O_2 diffusion for the deep penetration of catalysts into the membrane. To enhance the hydrophobicity of the catalyst layer, Xu et al. [9] added PTFE into the conventional hydrophilic catalyst layer and annealed the catalyst layer at 340 °C. However, annealing catalyst layer at temperature higher than 270 °C can lead to the decomposition of the side chains of Nafion and consequently decrease proton conductivity of catalyst layer [17].

In this work, we prepared the cocrystallized CCM by together crystallizing amorphous Nafion membrane and catalyst layers at 120 °C. The resulting CCM reinforced the bonding between membrane and catalyst layers and increased the hydrophobicity of the catalyst layers. Serial cell tests indicated that the cocrystallized CCM had much better performance than the conventional CCM.

2. Experimental

2.1. Preparation of Nafion membrane and cocrystallized CCM

The cocrystallized CCM was prepared by together crystallizing amorphous Nafion membrane and catalyst layers. The details of casting Nafion membrane and fabricating the cocrystallized CCM are described as follows.

Firstly, the Nafion solution (5 wt.%, Du Pont) was heated at 60 °C for 10 h to remove the solvent. Then the obtained Nafion ionomer was redissolved in N,N-dimethylacetamide (DMAc) with 10 wt.% of Nafion content. The Nafion/DMAc solution was cast onto a flat glass substrate and dried at 60 °C for 35 h. The thickness of the obtained amorphous membrane was about 120 μm . For comparison, the crystallized membrane was prepared by annealing the amorphous Nafion membrane at 120 °C and vacuum for 4 h. All Nafion membranes were successively pre-treated by 5 vol.% H_2O_2 and 0.5 mol L^{-1} H_2SO_4 , and then rinsed with the deionized water.

Iridium black (Johnson Matthey) and Pt/C (70 wt.%, Johnson Matthey) were used as the anode and cathode catalysts, respectively. Homogeneous ink consisting of catalyst (iridium black or Pt/C), Nafion solution (5 wt.%, Du Pont) and isopropanol was sprayed onto

the amorphous membrane to form the catalyst layers. After being dried at 80 °C under vacuum for 1 h, the CCM was cocrystallized at 120 °C under vacuum for 4 h. This cocrystallized CCM was denoted as CCM-1. For comparison, another two conventional CCMs, CCM-2 and CCM-3, were made by the same procedure, except that their catalyst layers were sprayed on home-made crystallized membrane and commercial Nafion 115 membrane (Du Pont), respectively, and that they did not undergo the cocrystallization treatment. The catalyst loading of all the CCMs was about 2.0 mg cm^{-2} for iridium black and 1.0 mg cm^{-2} for Pt/C.

2.2. Physical characterization of CCM

JSM 6360-LV and NOVA NanoSEM 450 Scanning electron microscope (SEM) were employed to observe the cross-sections and surfaces of the CCMs, respectively. Destructive test was conducted by soaking the MEA in anhydrous ethanol. X-ray diffraction (XRD) patterns were recorded on Rigaku D/MAX 2500/PC X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm). The contact angle on the anode surface of CCM was measured by the KRÜSS DSA100 Drop Shape Analysis System.

2.3. Evaluation of water electrolysis performance

Porous titanium (Pt plated, 0.7 mm in thickness) and wet-proof carbon paper (Toray, TGP-H-60) served as the anode and cathode diffusion layer, respectively. The CCM and the carbon paper were hot pressed together at 120 °C and 0.5 MPa for 1 min. A home-made electrolysis test stand was used to evaluate the performance of the CCM. The SPE water electrolyser performance was evaluated at atmosphere pressure and 80 °C. Electrochemistry impedance spectroscopy (EIS) was carried out at 1.45 V by Solartron 1287 Electrochemical Interface in conjunction with Solartron 1260 Frequency Response Analyzer in frequency from 0.1 Hz to 10 kHz [18]. The impedance diagrams were analyzed and modelled using the ZView program of Solartron, version 3.0. The stability tests were conducted under 2000 mA cm^{-2} at atmosphere pressure and 80 °C.

3. Results and discussion

Nafion membrane cast at low temperature (between room temperature and 80 °C) was essentially amorphous, and annealing it at temperature higher than its glass transition temperature (T_g , 100 °C) can fuse its fluorocarbon chains together and therefore increase crystallinity of membrane [19, 20]. However, fabricating the CCM at a higher temperature may decrease the proton conductivity of Nafion. Therefore, the thermal treatment of CCM should be carefully controlled at a temperature lower than 140 °C [21]. Thus, we cast the amorphous Nafion membrane at 60 °C, and further annealed it together with the catalyst layers at 120 °C under vacuum for 4 h to get the cocrystallized CCM-1, as described in Fig. 1. In the amorphous

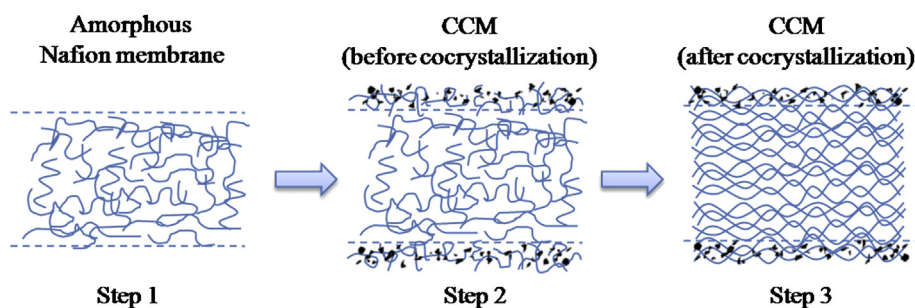


Fig. 1. Schematic illustration for the cocrystallized CCM fabrication.

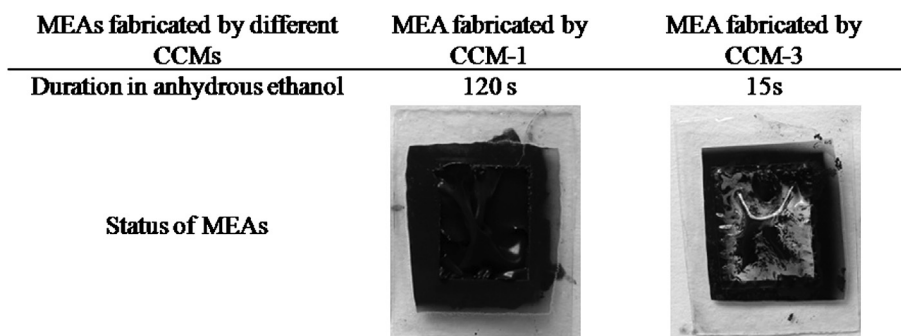


Fig. 2. Photographs of MEAs after being soaked in anhydrous ethanol.

Nafion membrane fabricated in step 1, the Nafion molecules formed single chain coiled structures and overlapped with each other [17]. In step 2, catalyst layers were sprayed on the amorphous Nafion membrane. The spraying process was conducted at room temperature, and the following drying temperature of the CCM was only 80 °C, lower than the T_g of Nafion, so the Nafion in catalyst layers was also amorphous. During the process of annealing the CCM at 120 °C (step 3), local segmental motion of Nafion molecules induces the intertwining (viz. cocrystallization) of Nafion in membrane and catalyst layers, to effectively enhance the adhesion between membrane and catalyst layers.

It is well known that Nafion membrane swells easier in ethanol than in water [19]. Therefore, to explore the bonding between membrane and catalyst layers rapidly, destructive test was conducted by soaking MEAs prepared with the cocrystallized CCM-1 and conventional CCM-3 in anhydrous ethanol, respectively. As shown in Fig. 2, the catalyst layers of the conventional CCM-3 peeled off from membrane just after being soaked in anhydrous ethanol for 15 s, but the cocrystallized CCM-1 did not show any delamination even after 120 s. In anhydrous ethanol, the dimension of Nafion membrane increases considerably due to the ethanol absorption, whereas the dimension changes of the catalyst layers are smaller for the existence of catalysts with rigid property. Consequently, when the conventional CCM-3 was immersed in anhydrous ethanol, the continuity between membrane and catalyst layers tended to be destroyed. However, the delamination of the cocrystallized CCM-1 was avoided because of the intertwining of Nafion molecules in membrane and catalyst layers during

cocrystallization treatment. The above results demonstrated that the cocrystallization treatment effectively strengthened the cohesion between membrane and catalyst layers.

The polarization curves of electrolyzers with CCM-1, CCM-2 and CCM-3 before and after stability tests are compared in Fig. 3. The stability tests have been conducted at 2000 mA cm⁻² and 80 °C for over 2700 min. The result showed that the cocrystallized CCM-1 exhibited much lower electrolysis voltage and better stability than the other two CCMs. At 2000 mA cm⁻² and 80 °C, the voltage of water electrolyser with CCM-1 before stability test was 1.777 V, about 0.09 V lower than the other two CCMs. The performance is much better than the results reported for SPE water electrolysis under the similar conditions [6,22,23]. After stability test, there was no increase in cell voltage for CCM-1, but the increased cell voltages of CCM-2 and CCM-3 were 10 mV and 15 mV, respectively.

To investigate the mechanism of performance improvement for the cocrystallized CCM, the impedance spectra of the three CCMs were carried out at 80 °C and 1.45 V. The equivalent circuit was presented by $LR_\Omega(R_1Q_1)(R_{ct}Q_{dl})$, where R_Ω , R_1 , R_{ct} , Q_1 , Q_{dl} and L are the ohmic resistance, mass transfer resistance of the catalytic film, charge transfer resistance, constant phase element, double layer capacitance and inductor, respectively. The simulating results have been summarized in Table 1. It can be seen that the cocrystallized CCM-1 had much lower resistance than the other two CCMs (more than 0.05 Ω cm² lower in both ohmic resistance (R_Ω) and charge transfer resistance (R_{ct})). Lower R_Ω is helpful to lower ohmic overpotential; smaller R_{ct} which means faster catalytic reaction rate contributes to decreasing charge transfer overpotential.

The cross-sectional SEM images of CCMs before and after stability tests conducted at 2000 mA cm⁻² for over 2700 min are shown in Fig. 4. Some gaps between the membrane and catalyst layers can be seen in CCM-2 (Fig. 4b) and CCM-3 (Fig. 4c) before stability tests. After stability tests, obvious delamination appeared in CCM-2 (Fig. 4e) and CCM-3 (Fig. 4f) because of large amount of gas generation in the catalyst layers during water electrolysis and nonuniformity of compression force between the land and under the channel [14]. However, there were no gaps in the cocrystallized CCM-1 before (Fig. 4a) and even after stability test (Fig. 4d). It meant that the cocrystallized CCM had much stronger bonding between membrane and catalyst layers, which is consistent with the results of the destructive test. The increased bonding can (i)

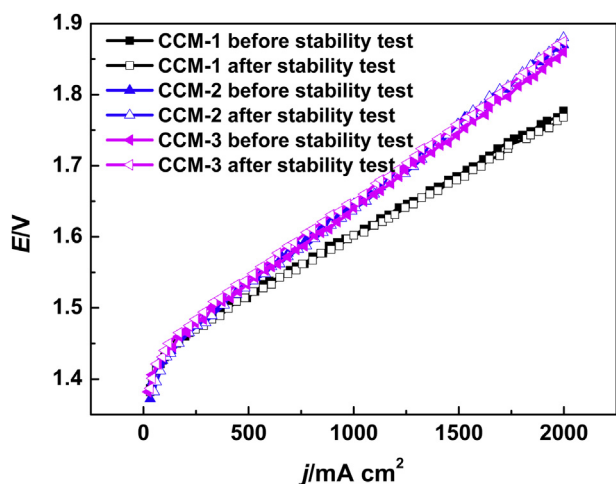


Fig. 3. Polarization curves of the three CCMs before and after 2700 min stability tests at 80 °C and atmosphere pressure.

Table 1

The simulating results of resistance for the SPE water electrolyzers.

Resistance	Electrolyser with CCM-1	Electrolyser with CCM-2	Electrolyser with CCM-3
R_Ω (Ω cm ²)	0.192	0.244	0.266
R_{ct} (Ω cm ²)	0.169	0.225	0.220

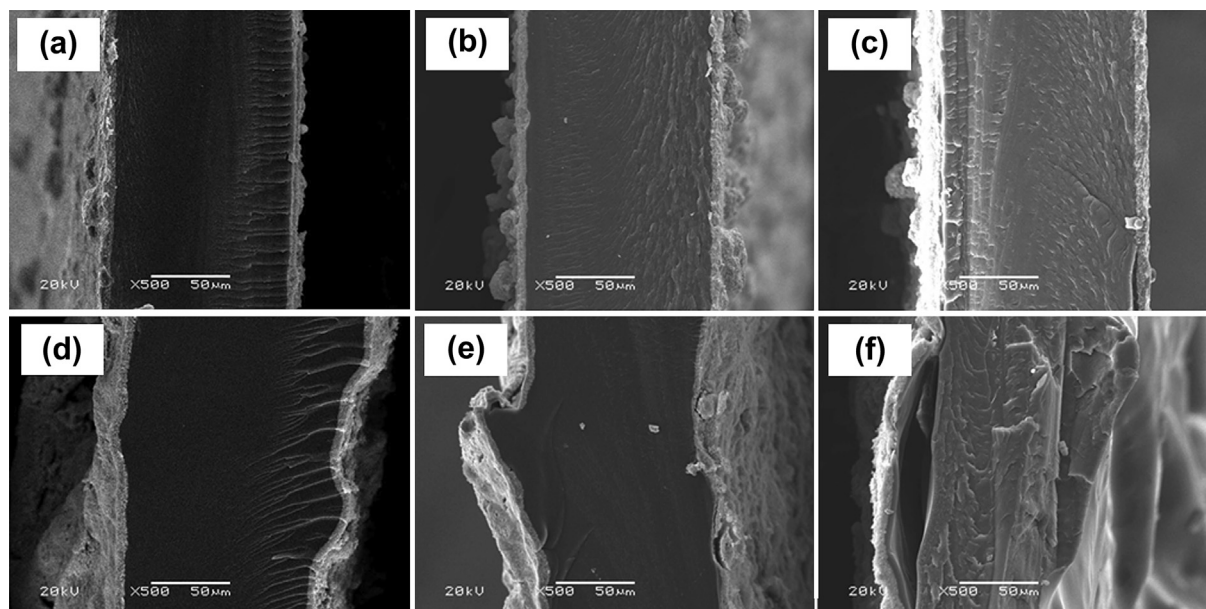


Fig. 4. Cross-sectional SEM images of CCMs before stability tests ((a) CCM-1, (b) CCM-2, (c) CCM-3) and after stability tests ((d) CCM-1, (e) CCM-2, (f) CCM-3).

lower the contact resistance between membrane and catalyst layers which can reduce the ohmic resistance (R_{Ω}), (ii) increase the triple-phase boundaries which is beneficial to decrease the charge transfer resistance (R_{ct}), and (iii) improve the stability of CCM.

The XRD patterns for the anode catalyst layers of CCM-1 and CCM-3 are shown in Fig. 5a. The mean crystal size of Ir black in the anode catalyst layers of CCM-1 and CCM-3, estimated from the broadening of the peak centred at 69.1° by the Debye–Scherrer equation, was 2.41 and 2.47 nm, respectively. It indicated that there was no obvious difference in the crystal size of Ir black between the cocrystallized CCM and the conventional CCM. Fig. 5b and c shows the SEM images of the anode catalyst layer surfaces of CCM-1 and CCM-3, respectively. The Ir black particles in the big agglomerations which were formed by Ir black and Nafion ionomer have been marked with circles. It can be seen that, compared with CCM-3,

there was no obvious change in the particle size of Ir black in CCM-1. Accordingly, the decrease in the charge transfer resistance (R_{ct}) of the cocrystallized CCM-1 cannot be attributed to the change of Ir catalyst.

To further study the reason for the improved performance of the cocrystallized CCM, the contact angles on the surfaces of anode catalyst layers of CCM-1, CCM-2 and CCM-3 were tested. As shown in Fig. 6, the contact angle on the surface of anode catalyst layer of CCM-1 was obvious larger than those of the other two CCMs, indicating the more hydrophobic anode surface of CCM-1. The improved hydrophobicity of CCM-1 can alleviate gas accumulation, thereby increase the real surface area of catalyst layers, and thus decrease the charge transfer resistance (R_{ct}) of the CCM, which is prone to enhance the catalytic reaction rate and lower the electrolysis voltage especially at high current densities [9].

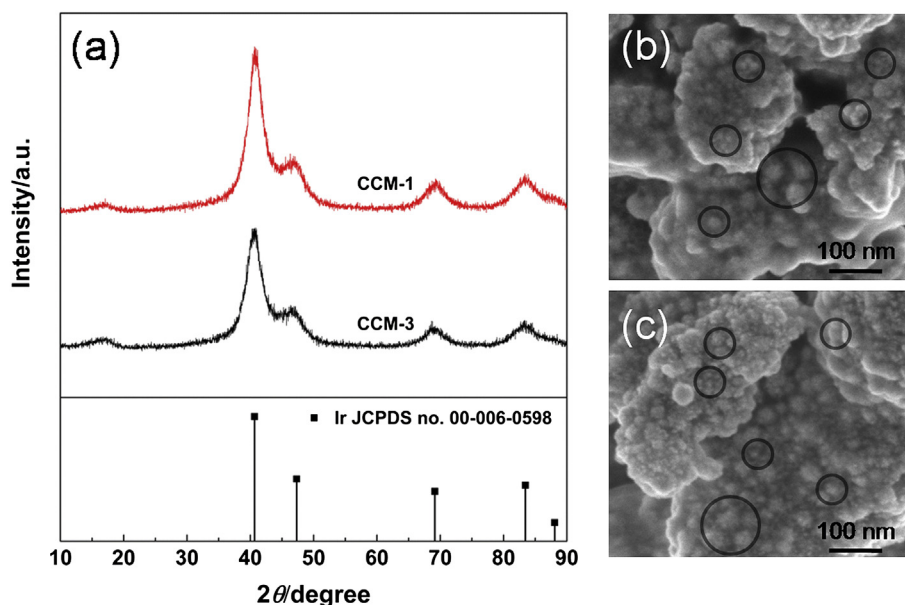


Fig. 5. (a) XRD patterns for the anode catalyst layers of CCM-1 and CCM-3, and SEM images for the anode catalyst layer surfaces of (b) CCM-1 and (c) CCM-3.

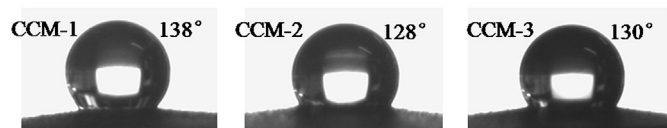


Fig. 6. Images of the contact angles on the surfaces of anode catalyst layers of the three CCMs.

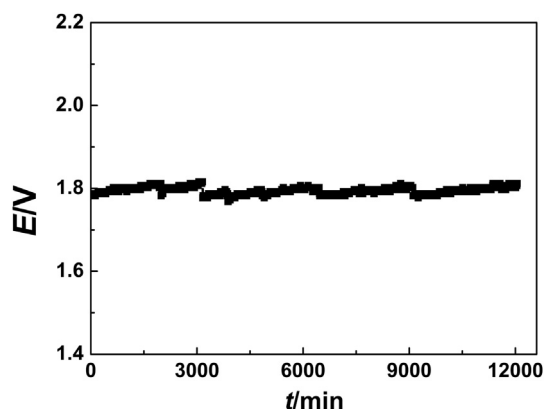


Fig. 7. Stability-test at 2000 mA cm^{-2} and 80°C for the electrolyser with cocrystallized CCM-1.

Furthermore, the stability test of CCM-1 has been carried out at 2000 mA cm^{-2} and 80°C for more than 12,000 min. It can be seen in Fig. 7 that there was no obvious increase in the electrolysis voltage after the stability test at such high current density. Based on above results and analyses, the high stability of CCM-1 is attributed to its stronger bonding between membrane and catalyst layers which can avoid the delamination of CCM. Besides, in respect that gas accumulation in catalyst layers can decrease the effective catalysis area and lead to the voltage increase, better gas transmission performance of catalyst layers of CCM-1 is also the reason for its stable performance.

4. Conclusion

Cocrystallized CCM was prepared by together crystallizing amorphous Nafion membrane and catalyst layers at 120°C . Study results indicated that the cocrystallization treatment not only

effectively reinforced the bonding between membrane and catalyst layers, but also increased the catalyst layers hydrophobicity, thus significantly decreased the resistance of CCM, enhanced catalytic reaction rate, and improved its stability. Therefore, the cocrystallization treatment is a promising way to improve the performance of SPE water electrolysis.

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